Supporting Information

Ligand-free Copper-catalyzed C–S Coupling of Aryl Iodides and Thiols

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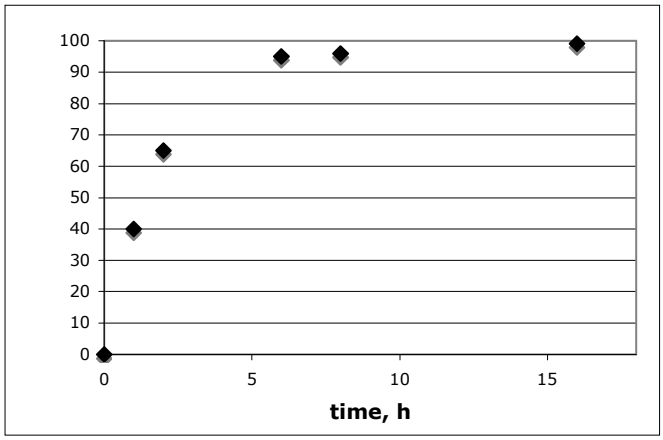
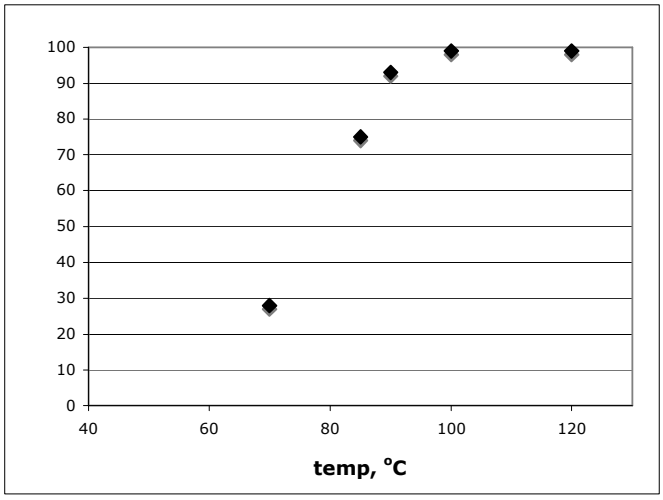
Chart 1. Time dependence of C–S coupling reaction catalyzed by CuI.



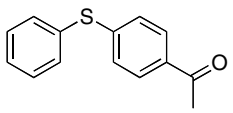
Reaction conditions: iodobenzene (5 mmol), thiophenol (6.5 mmol), K_2CO_3 (5.5 mmol), NMP (1 ml), CuI (2.5 mol%), T= 100 °C. Yield determined by GC using 100 μl dihexyl ether as external standard.

Chart 2. Temperature dependence of C–S coupling reaction catalyzed by CuI.



Reaction conditions: iodobenzene (5 mmol), thiophenol (6.5 mmol), K_2CO_3 (5.5 mmol), NMP (1 ml), CuI (2.5 mol%), t= 16 h. Yield determined by GC using 100 μl dihexyl ether as external standard.

Isolation of compounds is here reported for two representative examples. Products were purified via silica-gel column chromatography and characterized by ^{1}H-NMR and ^{13}C-NMR. (NMR spectra were recorded on a 400 MHz spectrometer at 298 K. The chemicals shifts (δ) are presented in ppm referenced to residual solvent resonances). For catalytic screenings, compounds were identified via gas chromatography and GC-mass spectrometry analysis. For confirmation of their identity, ^{1}H NMR analysis was performed on sample of some product mixtures (impure mixtures of desired product containing traces of diphenyldisulfides), after filtration through a plug of silica gel.



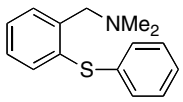
4-Phenylsulfanylacetophenone (table 5, entry 1)[1]

Column chromatography eluent (hexane/ethylacetate 9:1). Isolated as a yellow solid (89 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.55 (s, 3H), 7.19 (dt, J=7.00, 1.75 Hz, 2H), 7.39-7.41 (m, 3H), 7.48-7.50 (m, 2H), 7.82 (dt, J= 7.00, 1.75 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 26.9, 127.7, 127.8, 129.0, 129.3, 129.9, 132.4, 134.1, 145.1, 197.3.

HRMS (ES+) calcd for $C_{14}H_{12}OS$ ($[M+H]^+$) 229.0687, found 229.0654.



2-(*N,N*-dimethylbenzylamino)phenyl sulfide (table 6, entry 5)

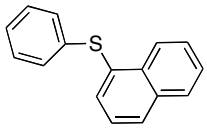
Column chromatography eluent (hexane/ethylacetate 5:1). Isolated as a yellow oil (83 %).

^{1}H NMR (400 MHz, CD_3OD): δ 2.26 (s, 6H,), 3.61 (s, 2H), 7.15-7.19 (m, 1H), 7.23-7.35 (m, 7H), 7.45-7.27 (d, 1H).

^{13}C NMR (100.576 MHz, CD_3OD): δ 139.9, 136.6, 136.1, 132.3, 131.2, 130.4, 129.4, 128.1, 127.2. 127.1, 62.3, 45.6.

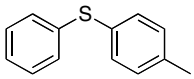
M/S (EI) m/z (relative intensity): 195 (72), 194 (68), 117 (34), 89 (100), 65 (70).

Anal. Calcld. for $C_{15}H_{17}NS$: C 74.03, H 7.04, N 5.76; Found: 73.94, H 7.10, N 5.69.



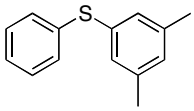
1-Naphthyl phenyl sulfide (table 5, entry 2)[2]

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.15-7.31 (m, 4H), 7.45-7.52 (m, 1H), 7.55-7.59 (m, 3H), 7.72-7.81 (m, 1H), 7.90-7.93 (m, 2H), 8.47-8.53 (m, 1H). HRMS (ES+) calcd for $C_{16}H_{12}S$ ($[M+H]^+$) 237.0738, found 237.0747.



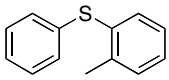
p-Tolylthiophenol (table 5, entry 3)[3]

Pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.15-7.36 (m, 9H), 2.37 (s, 3H). HRMS (ES+) calcd for $C_{13}H_{12}S$ ($[M]^+$) 200.0660, found 200.0667.



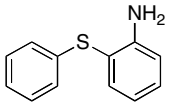
(3,5-dimethylphenyl) phenyl sulfide (table 5, entry 4)[3]

Pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28-7.46 (m, 5H), 7.14 (s, 2H), 7.0 (s, 1H). HRMS (ES+) calcd for $C_{14}H_{14}S$ ($[M]^+$) 214.0816, found 214.0828.



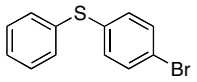
o-Tolylthiophenol (table 5, entry 5)

MS (EI) m/z (relative intensity): 200 (100) 185 (25) 122 (45) 91 (35). HRMS (ES+) calcd for $C_{13}H_{12}S$ ($[M]^+$) 200.0660, found 200.0634.



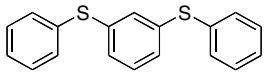
2-(phenylthio)aniline (table 5, entry 6)

MS (EI) m/z (relative intensity): 201 (100) 167 (30) 80 (30). HRMS (ES+) calcd for $C_{12}H_{11}NS$ ($[M+H]^+$) 202.0609, found 202.0694.



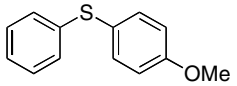
4-(bromophenyl)phenyl thioether (table 5, entry 7)

MS (EI) m/z (relative intensity): 264 (90) 266 (70) 184 (95) 185 (80) 92 (100). HRMS (ES+) calcd for $C_{12}H_9BrS$ ($[M]^+$) 263.9608, found 263.9613.



1,3-(bisphenylthio)benzene (table 5, entry 8)

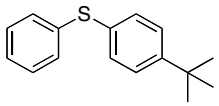
MS (EI) m/z (relative intensity): 294 (100) 184 (60). HRMS (ES+) calcd for $C_{18}H_{14}S_2$ ($[M]^+$) 294.0537, found 294.0529.



1-Methoxy-4-(phenylthio)benzene (table 6, entry 2)[3]

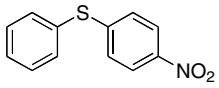
Column chromatography eluent (hexane). Isolated as a pale yellow oil (92 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (dt, J= 8.8 Hz, 2H), 7.15-7.28 (m, 5H), 6.93 (d, J=8.8 Hz, 2H), 3.83 (s, 3H). HRMS (ES+) calcd for $C_{13}H_{12}OS$ ($[M]^+$) 216.0609, found 216.0637.



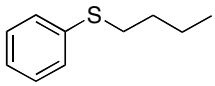
4-(*t*-buthylphenyl)phenyl sulfide (table 6, entry 3)

MS (EI) m/z (relative intensity): 242 (50) 227 (100) 117 (35) 99 (50). HRMS (ES+) calcd for $C_{16}H_{18}S$ ($[M]^+$) 242.1129, found 242.1159.



4-(nitrophenyl)phenyl sulfide (table 6, entry 4)

MS (EI) m/z (relative intensity): 231 (100) 184 (95) 152 (25). HRMS (ES+) calcd for $C_{12}H_9NO_2S$ ($[M+H]^+$) 232.0432, found 232.0422.



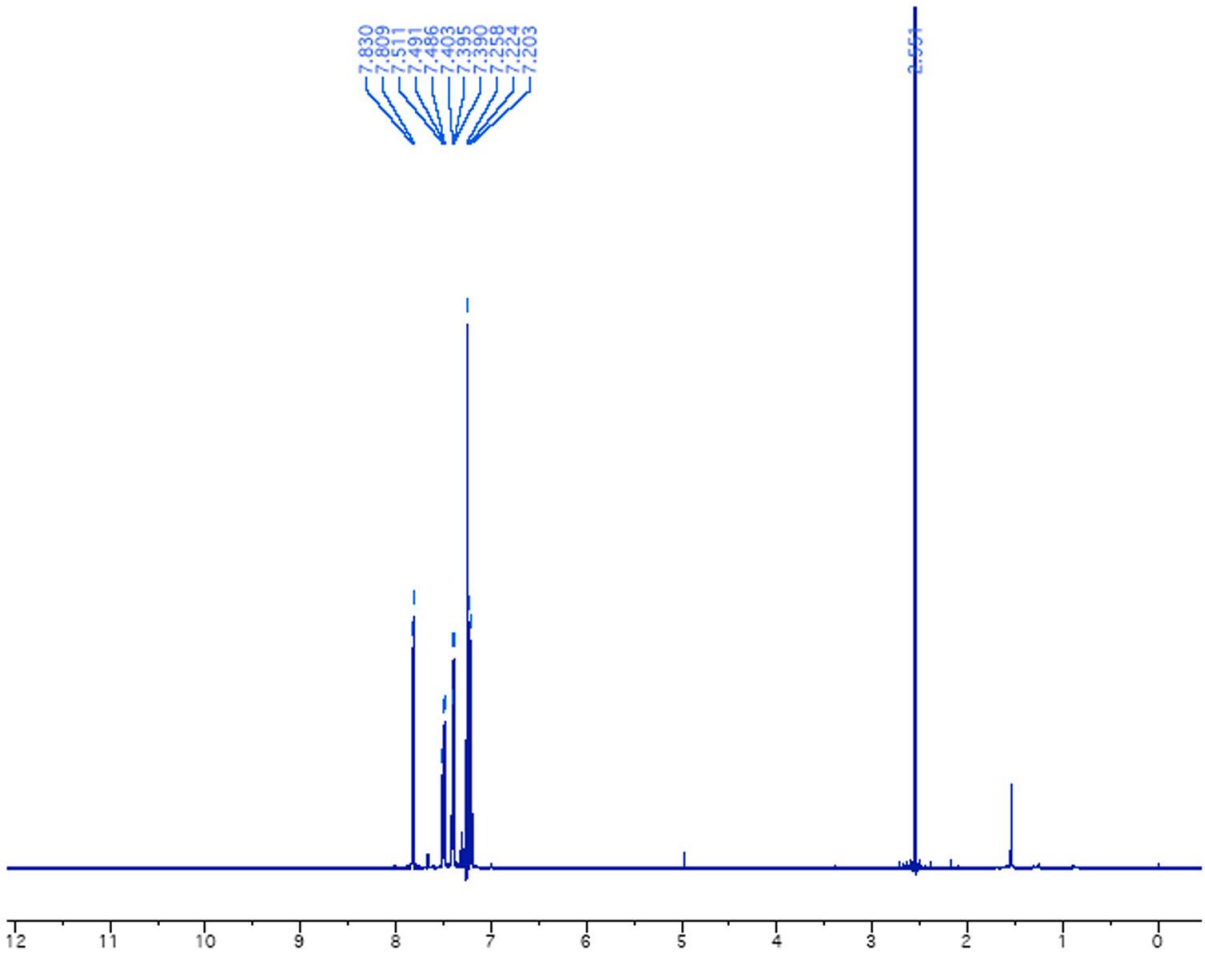
butyl-phenyl sulfide (table 6, entry 6)

MS (EI) m/z (relative intensity): 166 (32) 110 (100). HRMS (ES+) calcd for $C_{10}H_{14}S$ ($[M]^+$) 166.0816, found 165.0686.

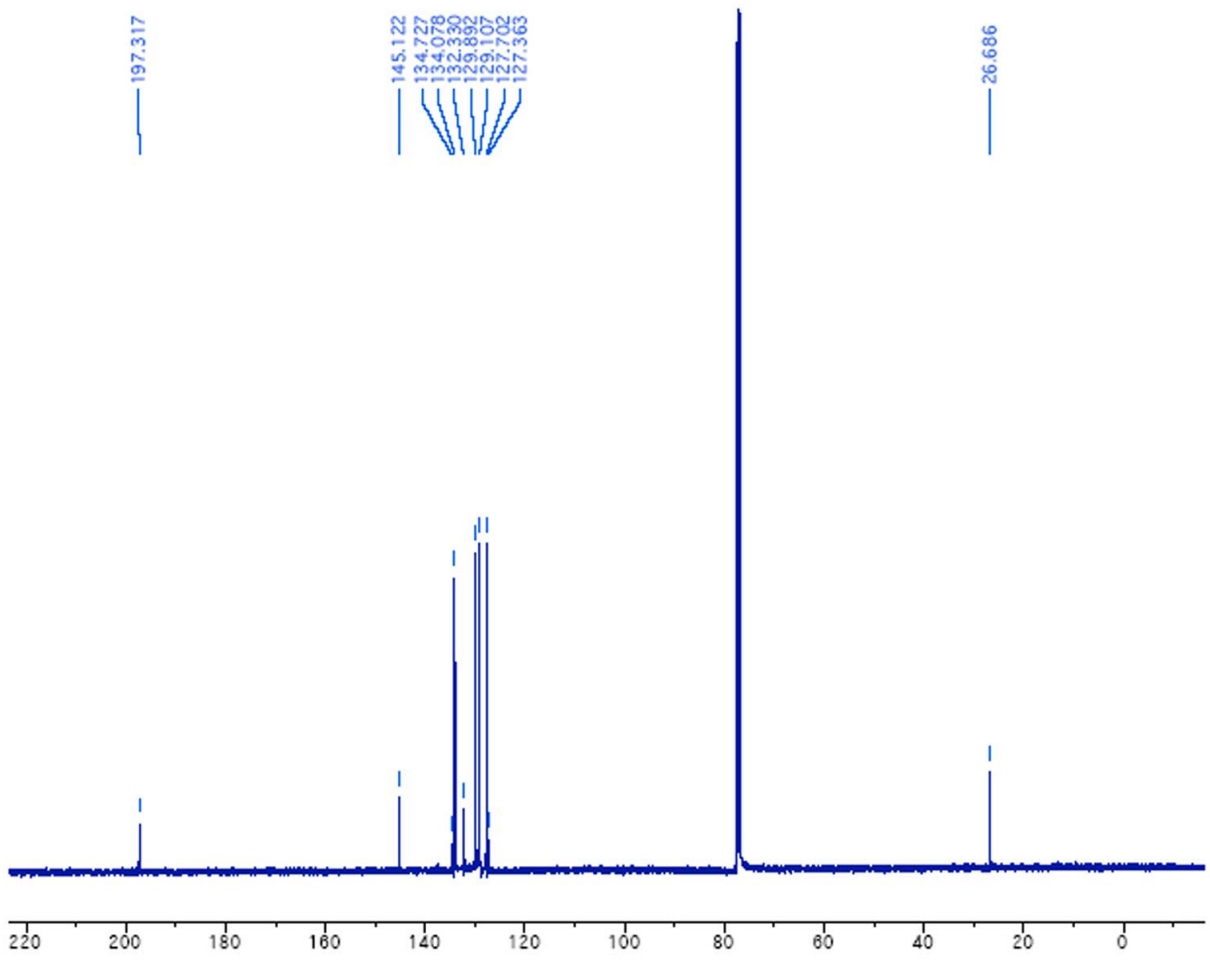
References

1. Y-C. Wong, T.T. Jayanth, C-H. Cheng *Org. Lett*. **2006**, *8* (24), 5613-5616.
2. T. Itoh, T. Mase, *Org. Lett*. **2004**, *6*, 4587-4590.
3. C. G. Bates, R. K. Gujadhur, D. Venkataraman *Org. Lett*. **2002**, *4* (16), 2803-2806.

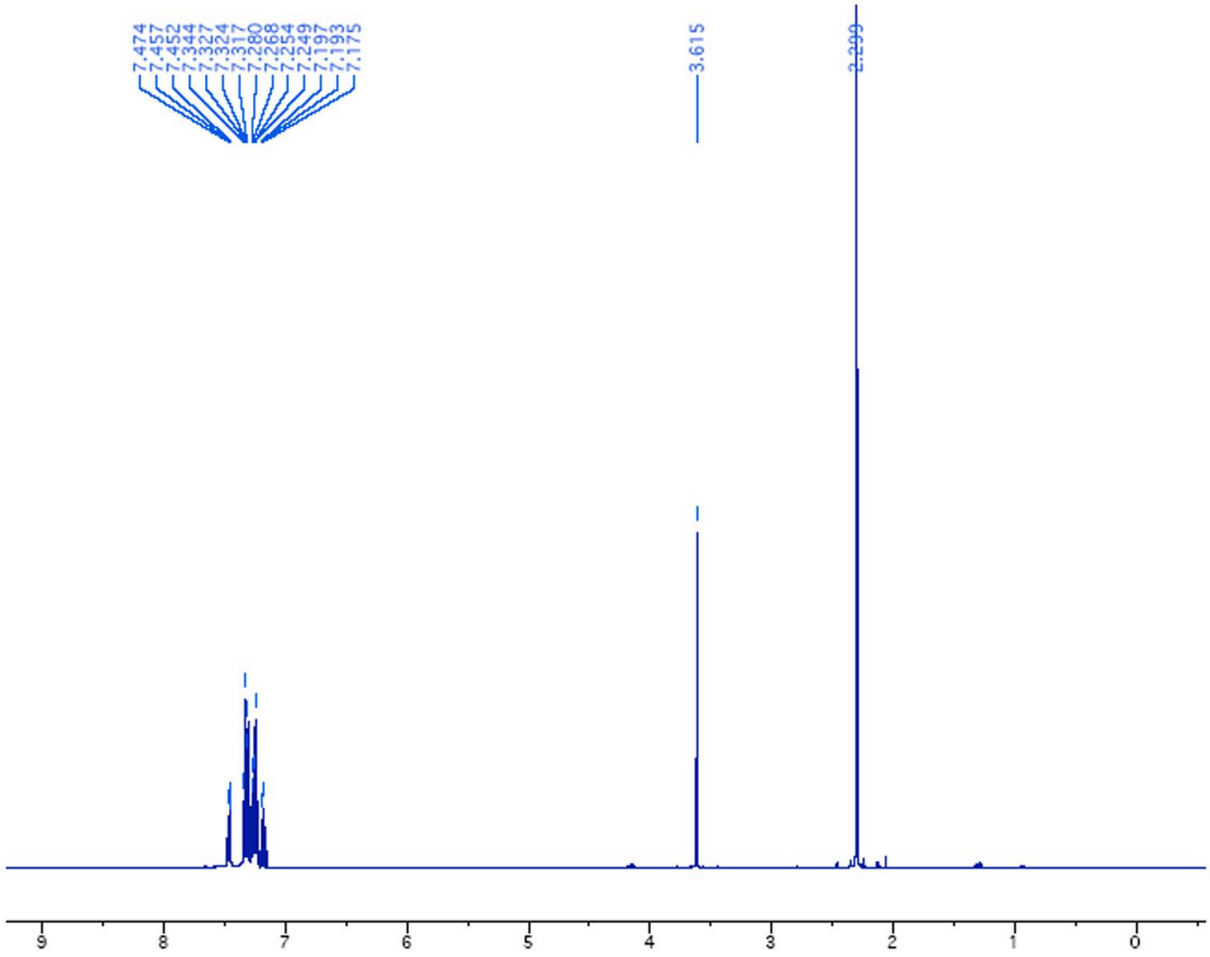
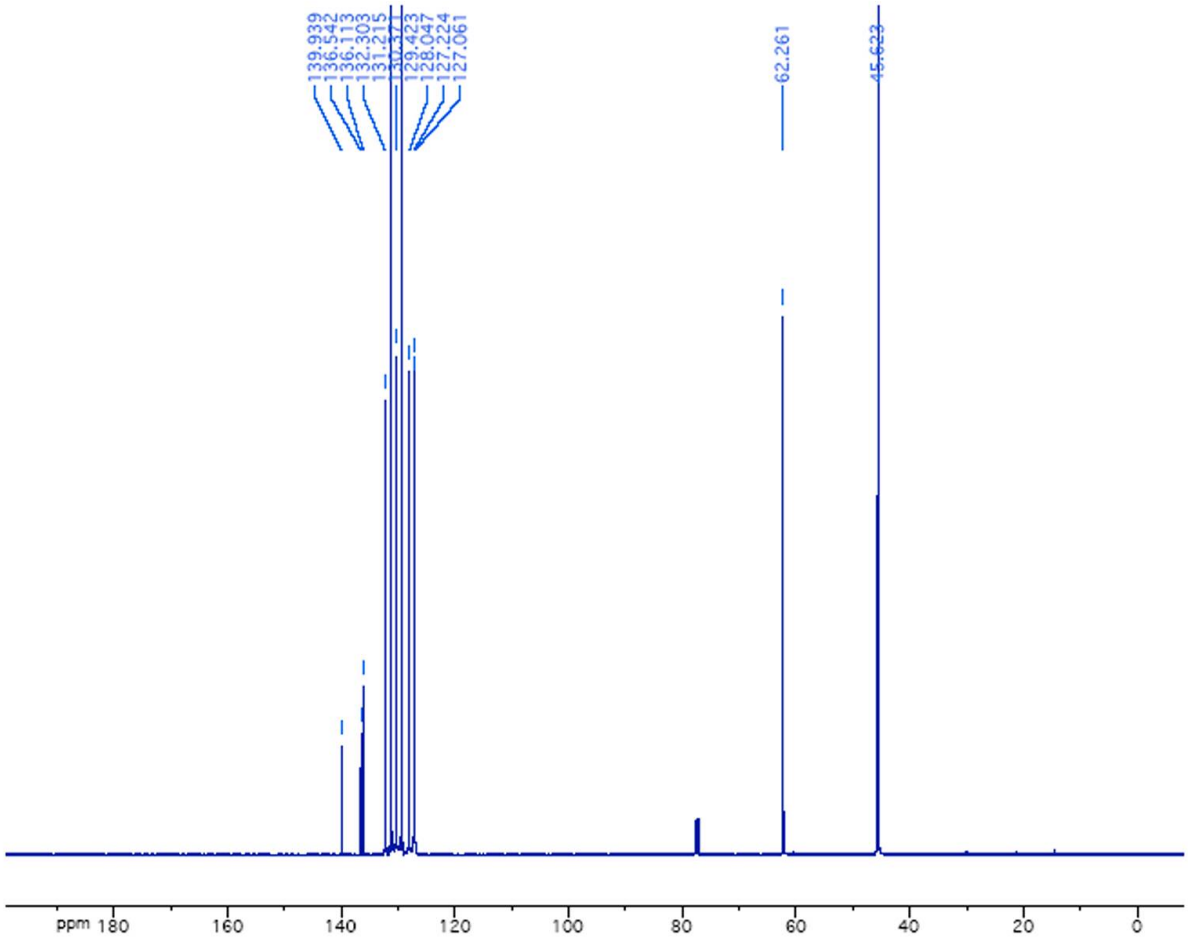
^{1}H-NMR for 4-Phenylsulfanylacetophenone (table 5, entry 1)



^{13}C-NMR for 4-Phenylsulfanylacetophenone (table 5, entry 1)



^{1}H-NMR for 2-(*N,N*-dimethylbenzylamino)phenyl sulfide (table 6, entry 5)



^{13}C-NMR for 2-(*N*,*N*-dimethylbenzylamino)phenyl sulfide (table 6, entry 5)